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Functional derivatives of (bi)phenyl-substituted carbazoles as building blocks for electro-active polymers

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ABSTRACT

(Bi)phenyl-substituted carbazoles containing reactive functional groups were synthesized by the multi-step synthetic rout. The monomers were examined by various techniques including thermogravimetry, differential scanning calorimetry, UV and fluorescence spectrometry as well as electron photoemission technique. These derivatives were also tested as hole transporting materials in bilayer OLEDs with Alq_3 as the emitter. The devices exhibited promising overall performance with a turn-on voltage of ~3 V, a maximal photometric efficiency of 5.1 cd/A and maximum brightness of 12,200–15,600 cd/m^2.

1. Introduction

Charge-transporting organic materials capable of forming amorphous films are favoured for various applications such as of electrophotographic devices [1], organic light emitting diodes (OLEDs) [2,3], photovoltaic cells [4] and photorefractive materials [5,6].

Carbazole-containing polymers and low-molecular-weight derivatives are among the most studied materials for optoelectronic and electronic applications due to their high hole mobility and excellent photoconductive properties [7]. Some carbazole based materials have been commercialized in a number of devices and processes (photocopy machines, laser printers, etc.) [8]. We have synthesized series of hole-transporting carbazole and indolo[3,2-b]carbazole derivatives [9,10]. We have observed that phenyl substituted indolo[3,2-b]carbazole-based derivatives demonstrate better charge transporting properties than the derivatives containing unsubstituted indolo[3,2-b]carbazole fragments [11].

In this work, we have designed and synthesized phenyl or biphenyl-substituted carbazole derivatives, which were expected to show enhanced hole injection and transport properties. On the other hand, the compounds contain reactive oxetanyl moieties and could be polymerized in solution to yield electro-active polymers.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using a Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys™ 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [12]. The measurement method was, in principle, similar to that described by Miyamoto et al. [13]. The samples for the ionization potential measurements were prepared as follows [14]. The materials were dissolved in THF and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of this layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during the measurements. The thickness of the layers was 0.5–1 μm.

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The multilayer electroluminescent devices were fabricated on glass substrates and had the typical structure with the organic layers sandwiched between a bottom ITO anode and a top metal cathode. Before use in device fabrication, the ITO-coated glass substrates were carefully cleaned and treated with UV/ozone right before deposition of the organic layers. PEDOT layers were deposited by spin-coating and heated at 120 °C for 30 min. It was described earlier that these conditions are suitable for preparation of PEDOT layers with optimum electrical properties [15]. The hole transporting layers (HTL) were prepared by spin-coating a 25 nm layer of the derivatives **5** or **7**. Tris(quinolin-8-olato)aluminium (Alq_3) was used as green light emitter. Evaporation of Alq_3 as well as of LiF/Al cathode was done at a pressure of 3×10^{-6} mbar in vacuum evaporation equipment.

The current–voltage and luminance–voltage characteristics were recorded under forward bias using a computer controlled Keithley 2400 source meter and a PR650 Spectrometer. All measurements were performed at ambient conditions in air [16].

2.2. Materials

9H-carbazole, 4-biphenylboronic acid, phenylboronic acid 1,3-propanediol ester, bis(triphenylphosphine)palladium(II) dichloride **($Pd(PPh_3)_2Cl_2$)**, tetrabutylammonium hydrogen sulphate (TBAHS), Alq_3, K_2CO_3 and potassium hydroxide were purchased from Aldrich and used as received.

3-Bromomethyl-3-methyloxetane was received from Chemada Fine Chemicals and used without further purification.

3-Iodo-9H-carbazole (1) and 3,6-diiodo-9H-carbazole (2) were obtained by a procedure of Tucker [17].

3-Iodo-9-(3-methyloxetan-3-ylmethyl)carbazole (3) and 3,6-diiodo-9-(3-methyloxetan-3-ylmethyl)carbazole (4) were prepared by the reaction of 3-iodo-9H-carbazole (1) or 3,6-diiodo-9H-carbazole (2) with large excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of the phase transfer catalyst – TBAHS. The synthesis was described earlier [18,19].

2.2.1. 3-(4-Biphenyl)-9-(3-methyloxetan-3-ylmethyl)carbazole (5)

0.5 g (1.32 mmol) of 3-iodo-9-(3-methyloxetan-3-ylmethyl) carbazole (**3**), 0.39 g (2 mmol) of biphenyl-4-boronic acid, 0.064 g (0.09 mmol) of $PdCl_2(PPh_3)_2$ and 0.51 g (13.2 mmol) of powdered potassium carbonate were stirred in 7 ml of THF containing water (0.25 ml) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate and the combined extract was dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:1) as an eluent. Yield: 0.4 g (76%) of white crystals. M.p.: 228–229.5 °C.

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.33–8.11 (m, 2H, Ar), 7.74–7.20 (m, 14H, Ar), 4.76 (d, 2H, CH_2 of oxetane ring, J = 6 Hz), 4.44 (s, 2H, CH_2N), 4.34 (d, 2H, CH_2 of oxetane ring, J = 6 Hz), 1.43 (s, 3H, CH_3). MS (APCI$^+$, 20 V), m/z (%): 404.5 ($[M+H]^+$, 100). IR (KBr, ν, cm^{-1}): 3051 (aromatic C–H), 2955; 2866 (aliphatic C–H), 1477; 1461 (C–N), 977 (C–O–C in oxetane ring), 808, 766(CH=CH of phenyl group).

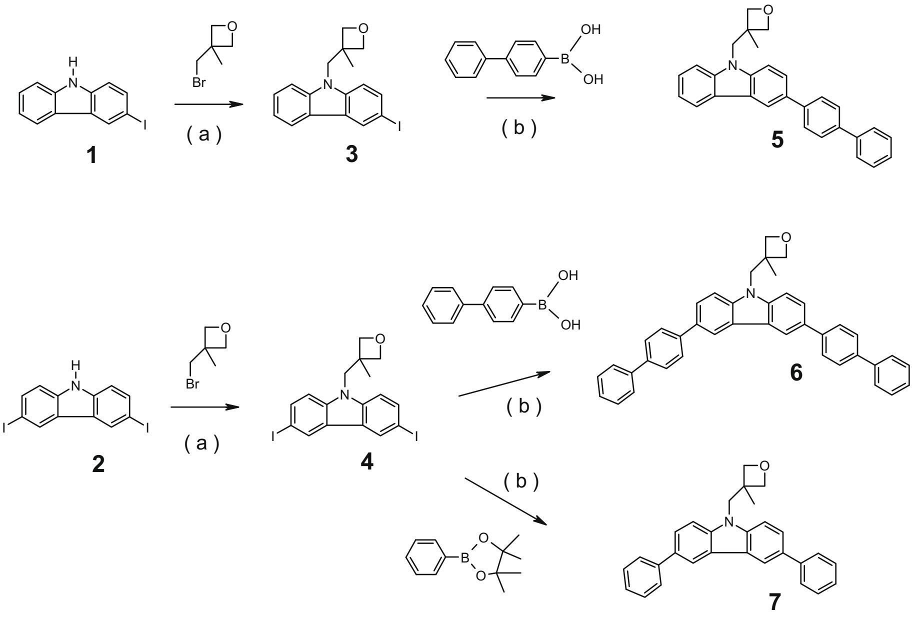
2.2.2. 3,6-Di(4-biphenyl)-9-(3-methyloxetan-3-ylmethyl)carbazole (**6**).

0.5 g (1 mmol) of 3,6-diiodo-9-(3-methyloxetan-3-ylmethyl)carbazole (**4**), 0.6 g (3 mmol) of biphenyl-4-boronic acid, 0.05 g (0.07 mmol) of $PdCl_2(PPh_3)_2$ and 0.4 g (10 mmol) of powdered potassium carbonate were stirred in 5 ml of THF containing water (0.25 ml) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:1) as an eluent. Yield: 0.3 g (54%) of white crystals. M.p.: 248–249 °C.

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.43 (s, 2H, Ar), 7.83–7.65 (m, 14H, Ar), 7.51–7.33 (m, 8H, Ar), 4.82 (d, 2H, CH_2 of oxetane ring, J = 7 Hz), 4.52 (s, 2H, CH_2N), 4.41 (d, 2H, CH_2 of oxetane ring, J = 7 Hz), 1.50 (s, 3H, CH_3). MS (APCI+, 20 V), m/z (%): 556 ($[M+H]^+$, 100). IR (KBr, ν, cm^{-1}): 3052 (aromatic C–H), 2955; 2867 (aliphatic C–H), 1476; 1461 (C–N), 978 (C–O–C in oxetane ring), 809, 766 (CH=CH of phenyl group).

2.2.3. 3,6-Diphenyl-9-(3-methyloxetan-3-ylmethyl)carbazole (**7**).

0.7 g (1.4 mmol) of 3,6-diiodo-9-(3-methyloxetan-3-ylmethyl)carbazole (**4**), 0.68 g (4.2 mmol) of phenylboronic acid



Scheme 1. (a) KOH, TBAHS and (b) $PdCl_2(PPh_3)_2$, K_2CO_3.

1,3-propanediol ester, 0.06 g (0.1 mmol) of $PdCl_2(PPh_3)_2$ and 0.54 g (14 mmol) of powdered potassium carbonate were stirred in 10 ml of THF containing water (0.5 ml) at 80 °C under nitrogen for 18 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:1) as an eluent. Yield: 0.35 g (62%) of white crystals. M.p.: 168–169.5 °C.

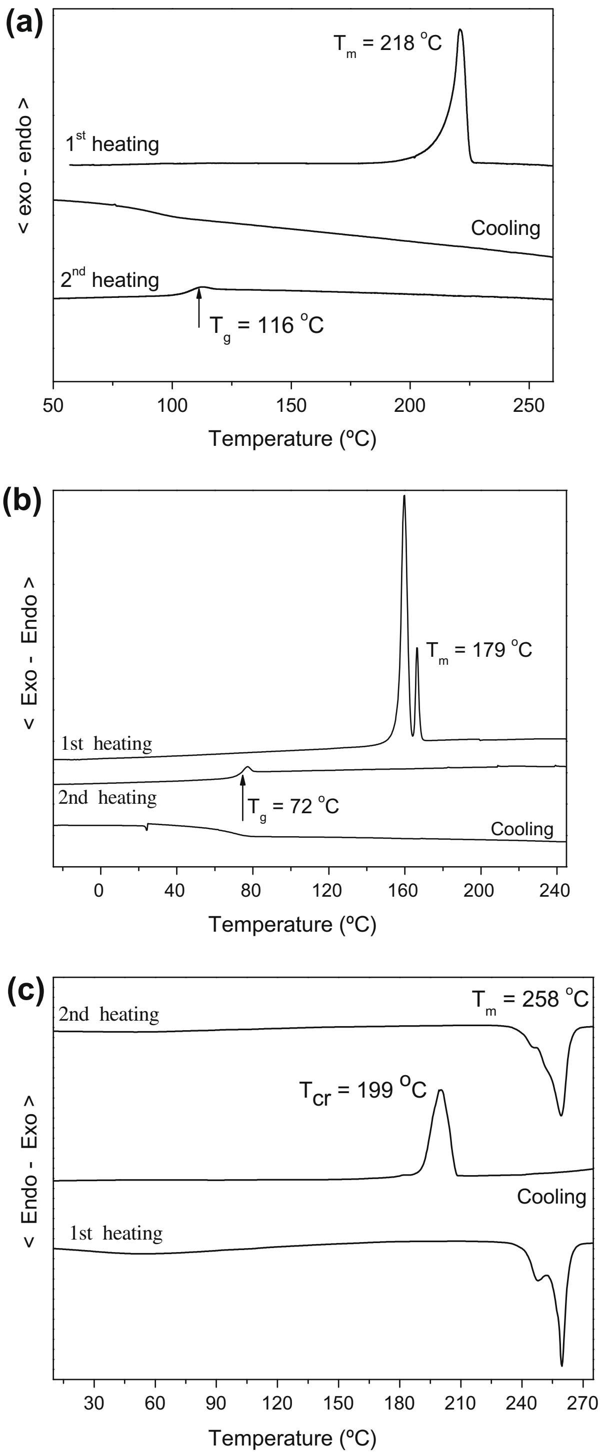


Fig. 1. DSC curves of compounds **5** (a), **7** (b) and **6** (c). Heating rate: 10 °C/min.

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.28 (s, 2H, Ar), 7.67–7.61 (m, 6H, Ar), 7.43–7.25 (m, 8H, Ar), 4.71 (d, 2H, CH_2 of oxetane ring, J = 7 Hz), 4.6 (s, 2H, CH_2N), 4.30 (d, 2H, CH_2 of oxetane ring, J = 7 Hz), 1.38 (s, 3H, CH_3). MS (APCI+, 20 V), m/z (%): 404 ($[M+H]^+$, 100). IR (KBr, ν, cm^{-1}): 3054 (aromatic C–H), 2959; 2867 (aliphatic C–H), 1476; 1462 (C–N), 978 (C–O–C in oxetane ring), 812, 762 (CH=CH of phenyl group).

3. Results and discussion

The synthesis of oxetanes containing phenyl- or biphenyl-substituted carbazole rings (**5**–**7**) was carried out by a multi-step synthetic route as shown in Scheme 1. Iodo-derivatives of carbazole (**1** and **2**) as key materials were synthesized from commercially available 9H-carbazole by Tucker iodination [17] with KI/KIO_3 in acetic acid. The compounds **1** and **2** were converted to oxetanyl-functionalized derivatives **3** and **4** by reaction with large excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of a phase transfer catalyst. The monomers **5**–**7** were obtained from 3-iodo-9-(3-methyloxetan-3-ylmethyl)carbazole or 3,6-diiodo-9-(3-methyloxetan-3-ylmethyl)carbazole by Suzuki reaction with derivatives of boronic acid, i.e. 4-biphenylboronic acid or phenylboronic acid 1,3-propanediol ester.

All the newly synthesized monomers were identified by mass spectrometry, IR-, and ^1H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials **5**–**7** were soluble in common organic solvents, such as chloroform and THF at room temperature. Transparent thin films

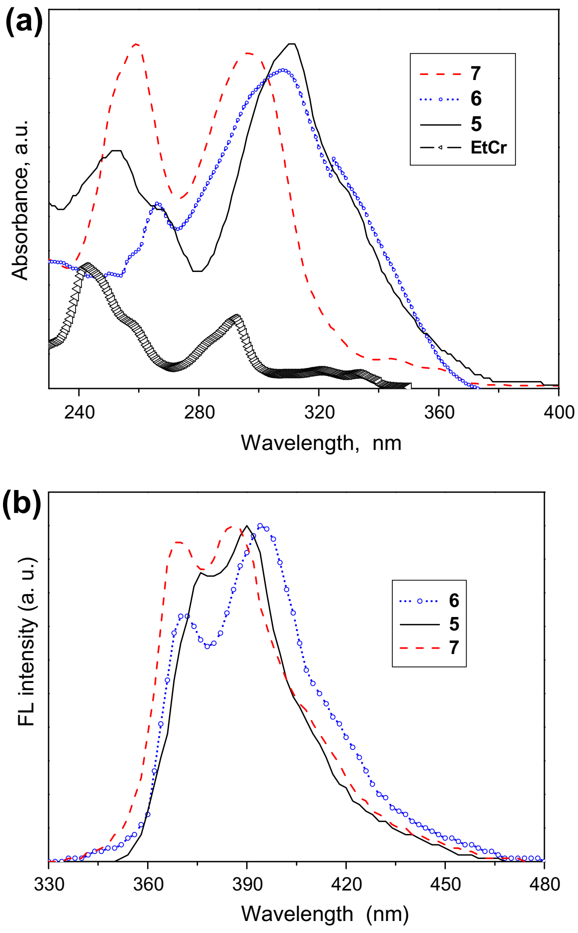


Fig. 2. UV absorption (a) and FL (b) spectra of dilute THF solutions of the compounds **5**–**7**, λ_{ex} = 290 nm.

of these materials could be prepared by spin-coating from solutions.

The behaviour under heating of compounds **5–7** was studied by DSC and TGA under a nitrogen atmosphere. The compounds demonstrated high thermal stability. The onsets of mass loss were 360 °C for **5**, 345 °C for **6** and 358 °C for **7**, as confirmed by TGA with a heating rate of 10 °C/min.

Compounds **5–7** were obtained as crystalline materials. When the crystalline samples were heated, endothermic peaks due to melting were observed in the region from 179 °C to 258 °C by DSC. However, the melt samples of **5** and **7** readily formed glasses when they were cooled on standing in air or with liquid nitrogen. The DSC thermo-grams of **7** are shown in Fig. 1b. When the crystalline sample of **7** was heated, an endothermic peak due to solid–solid phase transition was observed at 160 °C, where the crystals were transformed into a different crystal form. On further heating, the crystals melted at 179 °C to give an isotropic liquid. This is not the first observation of polymorphism in the compounds which are able to form glass. Earlier assumption of the different crystalline forms of the similar glass-forming materials was described by Shirota [20]. When the isotropic liquid was rapidly cooled, glass was formed. When the amorphous sample was heated, the glass-transition was observed at 72 °C, and on further heating no peaks due to crystallisation and melting appeared. The crystalline sample of compound **5** melted on first heating at 218 °C and formed glass (T_g = 116 °C) upon cooling (Fig. 1a).

Derivative **6** did not form glass. The DSC thermo-grams of **6** are shown in Fig. 1c. When the crystalline sample was heated, an endothermic melting peak was observed at 258°. When the melted sample was cooled, the crystallisation was observed at 199 °C to give the same crystals as obtained after synthesis, which melted at 258 °C.

UV absorption and FL spectra of dilute solutions of the compounds synthesized are shown in Fig. 2. For the comparison, the UV spectra of 9-ethylcarbazole (**EtCr**) are given in the fiure. Compounds **5**–**7** exhibit a broad absorption with λ_{max} in the range of 250–330 nm and demonstrate a red shift of the UV absorption with respect of that of **EtCr**. These red shifts show that phenyl or biphenyl-substituted carbazole core has more extended conjugation and that π electrons are de-localized over the fragments.

The FL emission spectra of the synthesized derivatives also show a red shift with respect of the **EtCr** spectrum [14]. The fluorescence spectra of **5**–**7** have similar shape, however the spectra of biphenyl substituted derivatives are slightly red shifted by ca. 3–6 nm. The analysis of the UV and FL spectra suggests that layers of (bi)phenyl-substituted carbazoles could have lower ionization potentials and better hole injection properties than that of derivatives containing unsubstituted carbazole rings [21].

The ionization potentials (I_p) of layers of the compounds synthesized were measured by the electron photoemission method. It was established that the I_p values of the layers range from 5.75 to 5.8 eV. It is evident that I_p of the derivatives are only slightly lower than that of compounds containing unsubstituted carbazole rings [22]. The I_p values demonstrate that these layers would be suitable for application in optoelectronic devices. Positive charges could be injected into the layers of **5**–**7** from compounds widely used in electrophotography, such as titanyl phthalocyanines, perylene derivatives, and bisazo pigments, which have I_p reaching 5.6 eV [23]. Compounds **5**–**7** can also be applicable as hole transporting (HT) layers in multilayer electroluminescent devices.

The derivatives 5 and 7, which form thin amorphous films, were tested in OLEDs as HT materials. The two layer OLED devices were prepared using these compounds for the HT layers and Alq_3 for the electroluminescent/electron transporting layers. PEDOT was used as a hole injecting layer. The cathode used was aluminium with a thin LiF electron injection layer. When a positive voltage was applied the bright green electroluminescence of Alq_3 was observed with an emission maximum at around 520 nm [24,25]. This implies that the hole mobility in the HT layers of 5 and 7 is fully sufficient for an effective charge carrier recombination occurring within the Alq_3 layer. No exciplex formation at the interface between HT and Alq_3 layer was observed.

Fig. 3 shows current–voltage and luminance–voltage characteristics as well as the efficiencies for the OLEDs containing the HTL of **5** and **7**. The characteristics of a device without HTL are presented for the comparison. The devices containing **5** or **7** exhibit turn-on

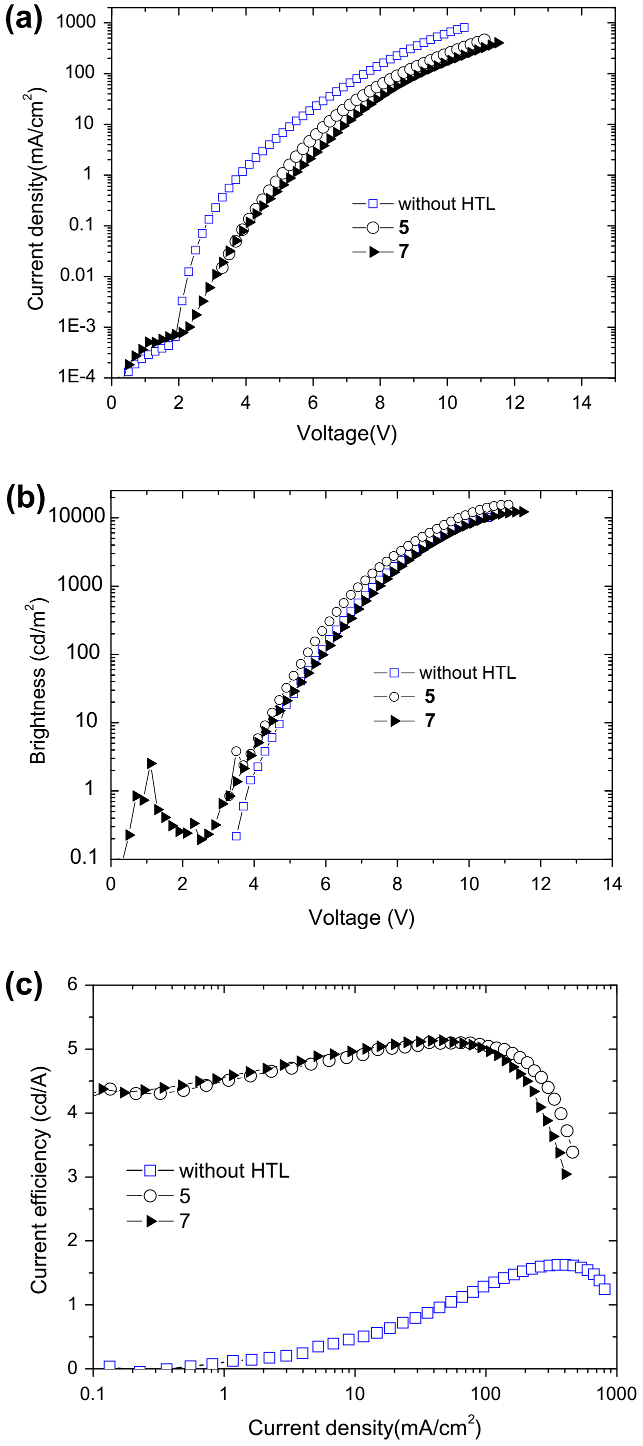


Fig. 3. OLED characteristics of the devices with the configuration: ITO/PEDOT/compound **5** or **7**/Alq_3/LiF/Al; (a) current density–voltage; (b) brightness–voltage; and (c) efficiency–current density plots.

voltages of ca. 3 V (defined as the voltage where electroluminescence becomes detectable), a maximum brightness of 12,200–15,600 cd/m^2 (at 11–12 V) and a photometric efficiency of about 5.1 cd/A. It should be stated that the efficiency of the devices shows an only a moderate drop in the observed current density window up to 200 mA/cm^2, for the technically important brightness of 100 cd/m^2, an efficiency above 4.5 cd/A is detected. These findings are rather promising also in comparison to similar Alq_3-based bilayer devices [26,27] as well as poly(N-vinylcarbazole)-based devices [28]. It should be pointed out that these characteristics were obtained in a non-optimized test device under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thicknesses and processing conditions [29].

In conclusion, functional derivatives of (bi)phenyl-substituted carbazole have been synthesized by a Suzuki-type aryl–aryl coupling. The monomers show a promising thermal stability. They have been tested as hole transporting layers in bilayer OLEDs with Alq_3 as the emitter. The devices exhibit good overall performance (turn-on voltage: ~3 V; maximum photometric efficiency: 5.1 cd/A; maximum brightness: 12,200–15,600 cd/m^2). These OLEDs properties are rather promising among Alq_3-based two-layer devices.

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